

SECTION 9.0

SOURCE TEST PROCEDURES

Benzene emissions from ambient air, mobile sources, and stationary sources can be measured utilizing the following test methods:²⁸³

- EPA Method 0030: Volatile Organic Sampling Train (VOST) with EPA Method 5040/5041: Analysis of Sorbent Cartridges from VOST;
- EPA Method 18: Measurement of Gaseous Organic Compound Emissions by Gas Chromatography;
- EPA method TO-1: Determination of Volatile Organic Compounds in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS);
- EPA method TO-2: Determination of Volatile Organic Compounds in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography/Mass Spectrometry;
- EPA Method TO-14: Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA® Passivated Canister Sampling and Gas Chromatographic (GC) Analysis;
- EPA Exhaust Gas Sampling System, Federal Test Procedure (FTP); and
- Auto/Oil Air Quality Improvement Research (AQIRP) Speciation Methodology.

If applied to stack sampling, the ambient air monitoring methods may require adaptation or modification. To ensure that results will be quantitative, appropriate precautions must be taken to prevent exceeding the capacity of the methodology. Ambient methods that

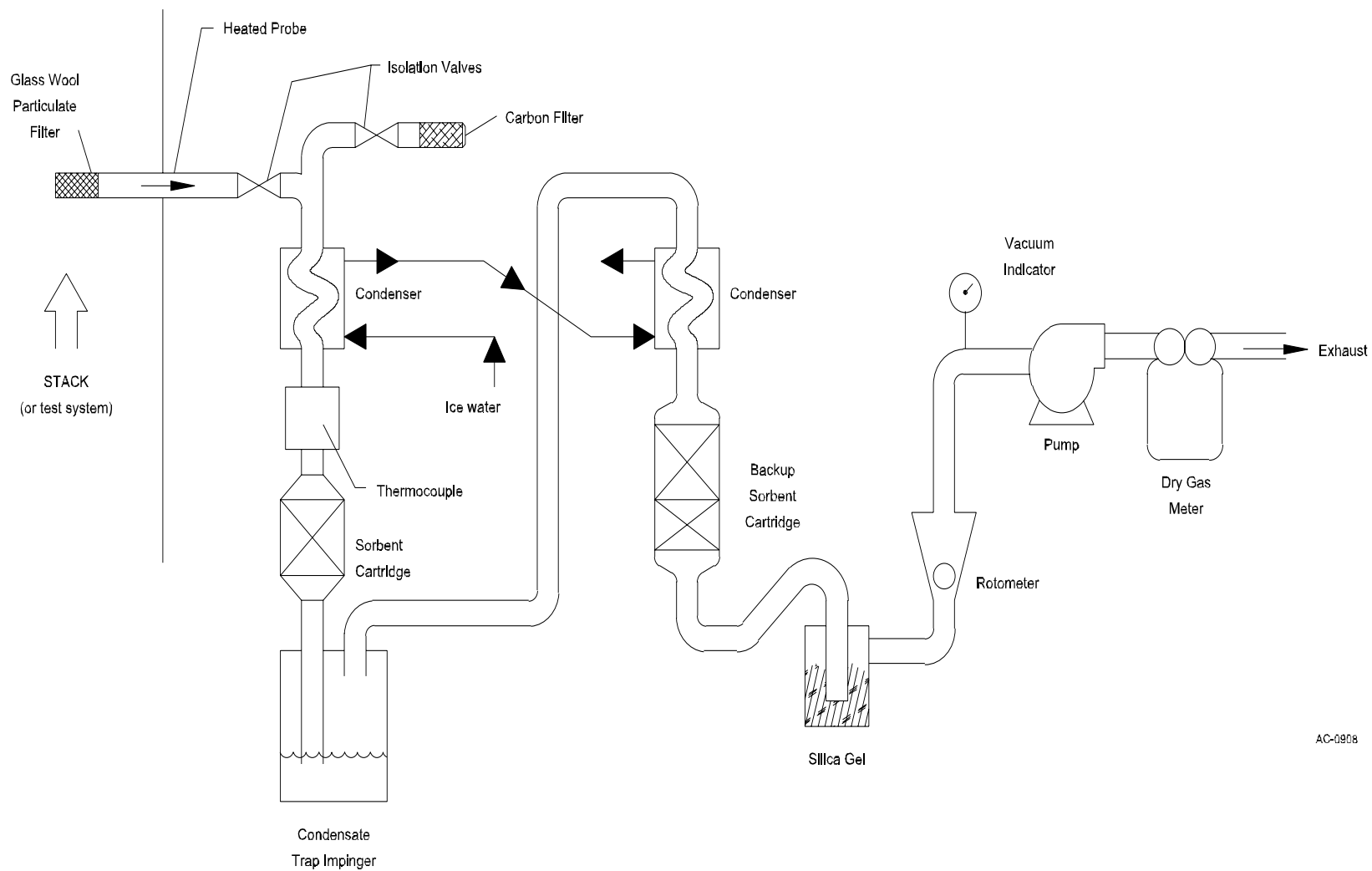
require the use of sorbents are susceptible to sorbent saturation if high concentration levels exist. If this happens, breakthrough will occur and quantitative analysis will not be possible.

9.1 EPA METHOD 0030²⁸⁴

The VOST from SW-846 (third edition) is designed to collect VOCs from the stack gas effluents of hazardous waste incinerators, but it may be used for a variety of stationary sources. The VOST method was designed to collect volatile organics with boiling points in the range of 30°C to 100°C. Many compounds with boiling points above 100°C may also be effectively collected using this method. Because benzene's boiling point is about 80.1°C, benzene concentrations can be measured using this method. Method 0030 is applicable to benzene concentrations of 10 to 100 or 200 parts per billion by volume (ppbv). If the sample is somewhat above 100 ppbv, saturation of the instrument will occur. In those cases, another method, such as Method 18, should be used. Method 0030 is often used in conjunction with analytical Method 5040/5041.

Figure 9-1 presents a schematic of the principal components of the VOST.²⁴¹ In most cases, 20 L of effluent stack gas are sampled at an approximate flow rate of 1 L/min, using a glass-lined heated probe. The gas stream is cooled to 20°C by passage through a water-cooled condenser and the volatile organics are collected on a pair of sorbent resin traps. Liquid condensate is collected in the impinger located between the two resin traps. The first resin trap (front trap) contains about 1.6 g Tenax® and the second trap (back trap) contains about 1 g each of Tenax® and petroleum-based charcoal (SKC lot 104 or equivalent), 3:1 by volume.

The Tenax® cartridges are then thermally desorbed and analyzed by purge-and-trap GC/MS along with the condensate catch as specified in EPA Methods 5040/5041. Analysis should be conducted within 14 days of sample collection.



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Figure 9-1. Volatile Organic Sampling Train (VOST)

Source: Reference 241.

The sensitivity of Method 0030 depends on the level of interferences in the sample and the presence of detectable levels of benzene in the blanks. Interferences arise primarily from background contamination of sorbent traps prior to or after use in sample collection. Many interferences are due to exposure to significant concentrations of benzene in the ambient air at the stationary source site and exposure of the sorbent materials to solvent vapors prior to assembly.

To alleviate these problems, the level of the lab blank should be determined in advance. Calculations should be made based on feed concentration to determine if blank level will be a significant problem. Benzene should not be chosen as a target compound at very low feed levels because it is likely there will be significant blank problems.²⁸³

One of the disadvantages of the VOST method is that because the entire sample is analyzed, duplicate analyses cannot be performed. On the other hand, when the entire sample is analyzed, the sensitivity is increased. Another advantage is that breakthrough volume is not greatly affected by humidity.

9.2 EPA METHODS 5040/5041^{283,284}

The contents of the sorbent cartridges (collected using EPA Method 0030) are spiked with an internal standard and thermally desorbed for 10 minutes at 80°C with organic-free nitrogen or helium gas (at a flow rate of 40 mL/min), bubbled through 5 mL of organic-free water, and trapped on an analytical adsorbent trap. After the 10-minute desorption, the analytical adsorbent trap is rapidly heated to 180°C, with the carrier gas flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The volatile organics are separated by temperature-programmed gas chromatography and detected by low-resolution mass spectrometry. The concentrations of the volatile compounds are calculated using the internal standard technique. EPA Methods 5030 and 8420 may be referenced for specific requirements for the thermal desorption unit, purge-and-trap unit, and GC/MS system.

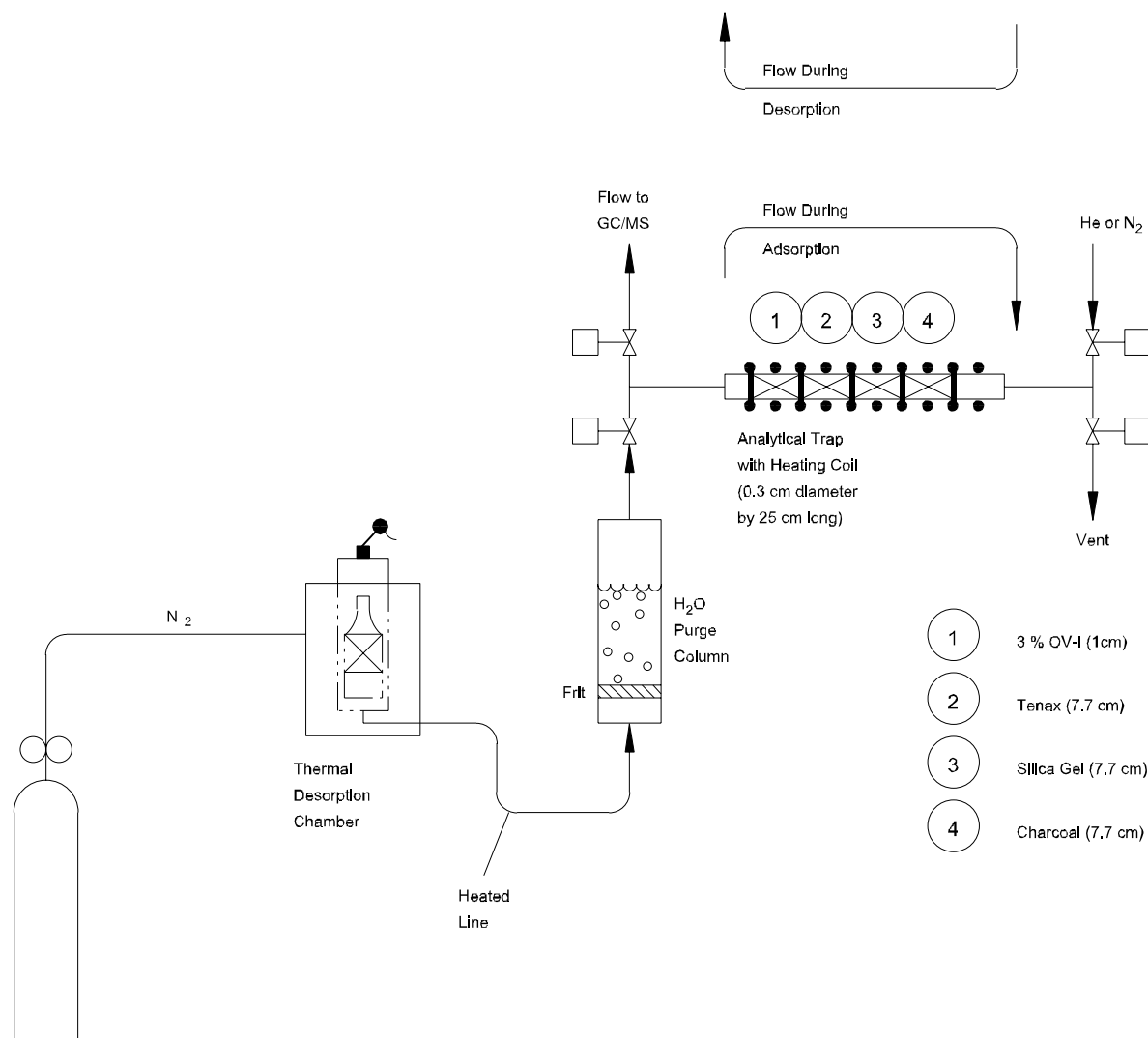
A diagram of the analytical system is presented in Figure 9-2. The Tenax® cartridges should be analyzed within 14 days of collection. The detection limits for low-resolution MS using this method are usually about 10 to 20 ng or 1 ng/L (3 ppbv).

The primary difference between EPA Methods 5040 and 5041 is the fact that Method 5041 utilizes the wide-bore capillary column (such as 30 m DB-624), whereas Method 5040 calls for a stainless steel or glass-packed column (1.8 x 0.25 cm I.D., 1 percent SP-1000 on 60/80 mesh Carbopack B).

9.3 EPA METHOD 18²⁸⁵

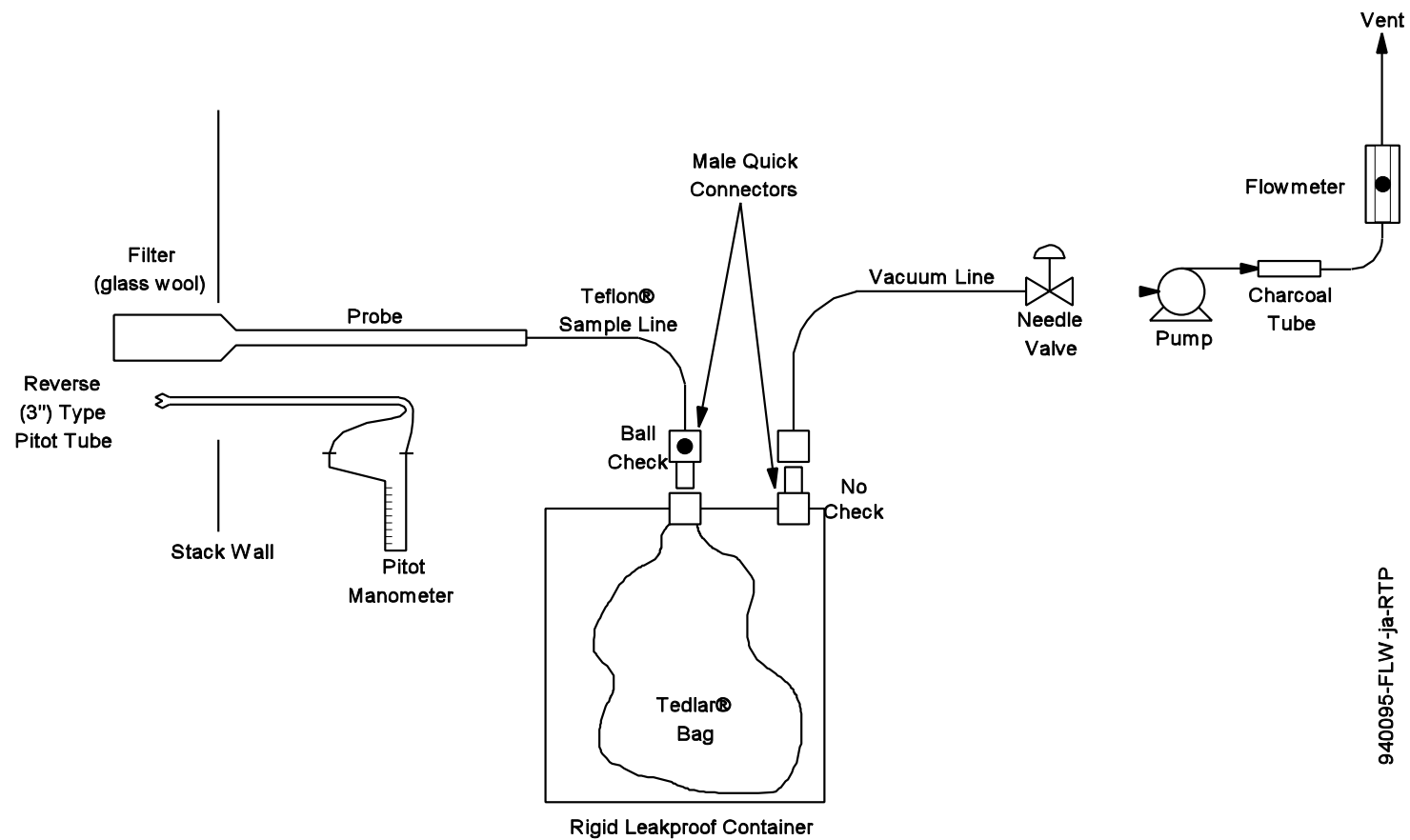
EPA Method 18 is the preferred method for measuring higher levels of benzene from a source (approximately 1 part per million by volume [ppmv] to the saturation point of benzene in air). In Method 18, a sample of the exhaust gas to be analyzed is drawn into a stainless steel or glass sampling bulb or a Tedlar® or aluminized Mylar® bag as shown in Figure 9-3.²⁸⁵ The Tedlar® bag has been used for some time in the sampling and analysis of source emissions for pollutants. The cost of the Tedlar® bag is relatively low, and analysis by gas chromatography is easier than with a stainless steel cylinder sampler because pressurization is not required to extract the air sample in the gas chromatographic analysis process.²⁸⁶ The bag is placed inside a rigid, leak-proof container and evacuated. The bag is then connected by a Teflon® sampling line to a sampling probe (stainless steel, Pyrex® glass, or Teflon®) at the center of the stack. The sample is drawn into the bag by pumping air out of the rigid container.

The sample is then analyzed by gas chromatography coupled with flame ionization detection. Based on field and laboratory validation studies, the recommended time limit for analysis is within 30 days of sample collection.²⁸⁷ One recommended column is the 8-ft x 1/8 in. O.D. stainless steel column packed with 1 percent SP-1000 in 60/80 carbopack B. However, the GC operator should select the column and GC conditions



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Figure 9-2. Trap Desorption/Analysis Using EPA Methods 5040/5041



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Figure 9-3. Integrated Bag Sampling Train

Source: Reference 285.

that provide good resolution and minimum analysis time for benzene. Zero helium or nitrogen should be used as the carrier gas at a flow rate that optimizes the resolution.

The peak areas corresponding to the retention times of benzene are measured and compared to peak areas for a set of standard gas mixtures to determine the benzene concentrations. The detection limit of this method ranges from about 1 ppm to an upper limit governed by the FID saturation or column overloading. However, the upper limit can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

The EPA's Atmospheric Research and Exposure Assessment Laboratory has produced a modified version of Method 18 for stationary source sampling.^{286,288} One difference from the original method is in the sampling rate, which is reduced to allow collection of more manageable gas volumes. By reducing the gas volumes, smaller Tedlar® bags can be used instead of the traditional 25-L or larger bags, which are not very practical in the field, especially when a large number of samples is required.²⁸⁶ A second difference is the introduction of a filtering medium to remove entrained liquids, which improves benzene quantitation precision.

The advantage of EPA Method 18 is that it is rapid and relatively inexpensive. However, it does require a fully equipped chromatography lab and a skilled analyst.

9.4 EPA METHOD TO-1 (COMPENDIUM)

Ambient air concentrations of benzene can be measured using EPA Method TO-1 from *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*.²⁸⁹ This method is used to collect and determine nonpolar, volatile organics (aromatic hydrocarbons, chlorinated hydrocarbons) that can be captured on Tenax® and determined by thermal desorption techniques. The compounds determined by this method have boiling points in the range of 80 to 200°C.

Method TO-1 can measure benzene concentrations from about 3 to 150 ppbv. The advantages and disadvantages are about the same as for the VOST method, and costs are comparable.

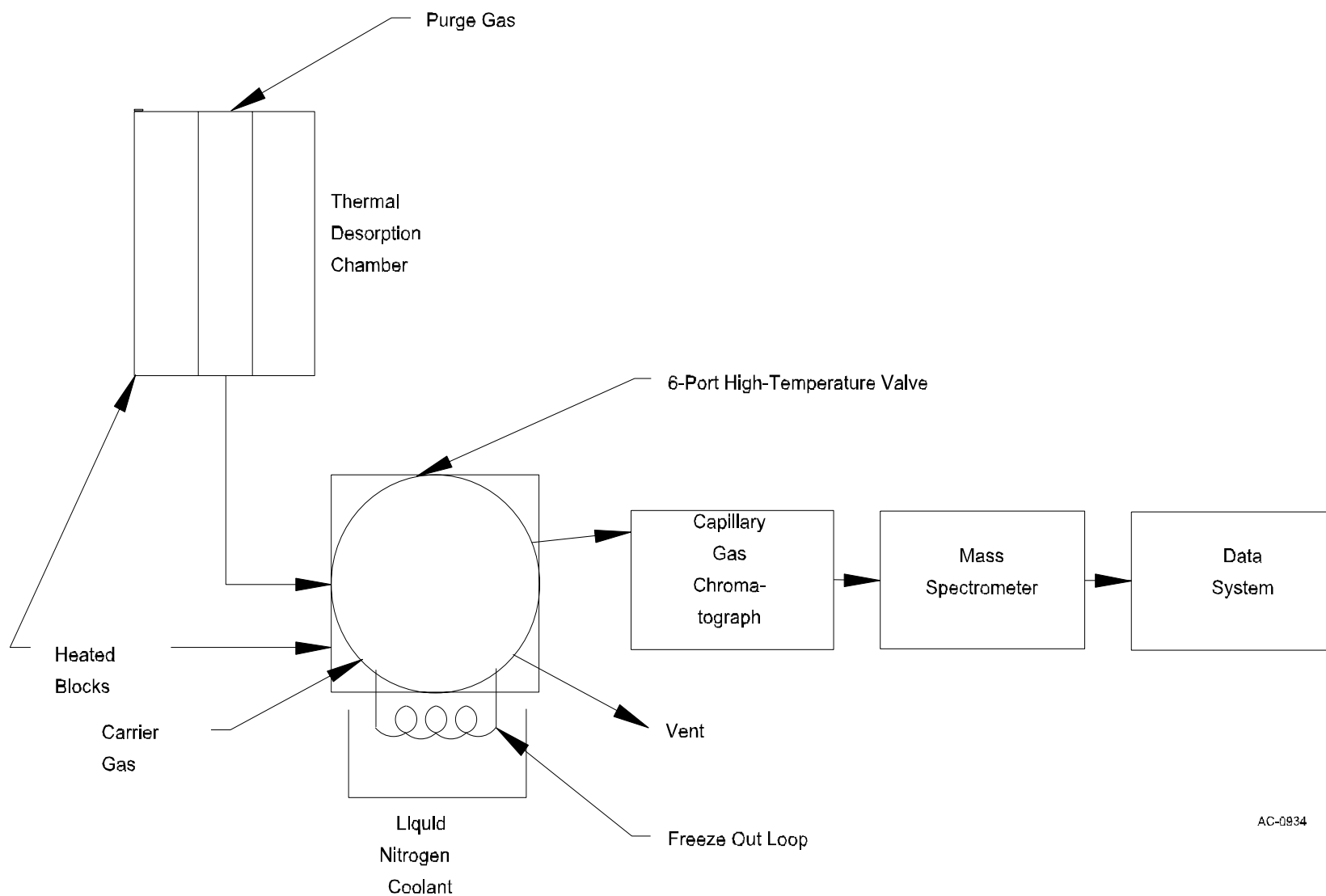
Figure 9-4 presents a block diagram of the TO-1 system. Figure 9-5 presents a diagram of a typical Tenax® cartridge.²⁸⁹ Ambient air is drawn through the cartridge, which contains approximately 1 to 2 grams of Tenax®. The benzene is trapped on the Tenax® cartridge, which is then capped and sent to the laboratory for analysis utilizing GC/MS according to the procedures specified in EPA Method 5040.

The exact run time, flow rate, and volume sampled varies from source to source depending on the expected concentrations and the required detection limit. Typically, 10 to 20 L of ambient air are sampled. Estimated breakthrough volume of Tenax® (for benzene) is 19 L/g at 38°C. Analysis should be conducted within 14 days of collection. A capillary column (fused silica SE-30 or OV-1) having an internal diameter of 0.3 mm and a length of 50 m is recommended. The MS identifies and quantifies the compounds by mass fragmentation or ion characteristic patterns. Compound identification is normally accomplished using a library search routine on the basis of GC retention time and mass spectral characteristics.

9.5 EPA METHOD TO-2^{283,289}

Method TO-2 is used to collect and determine highly volatile, non-polar organics (vinyl chloride, vinylidene chloride, benzene, toluene) that can be captured on a carbon molecular sieve (CMS) trap and determined by thermal desorption techniques. The compounds to be determined by this technique have boiling points in the range of 15 to 120°C. Method TO-2 has the same advantages and disadvantages as the VOST method.

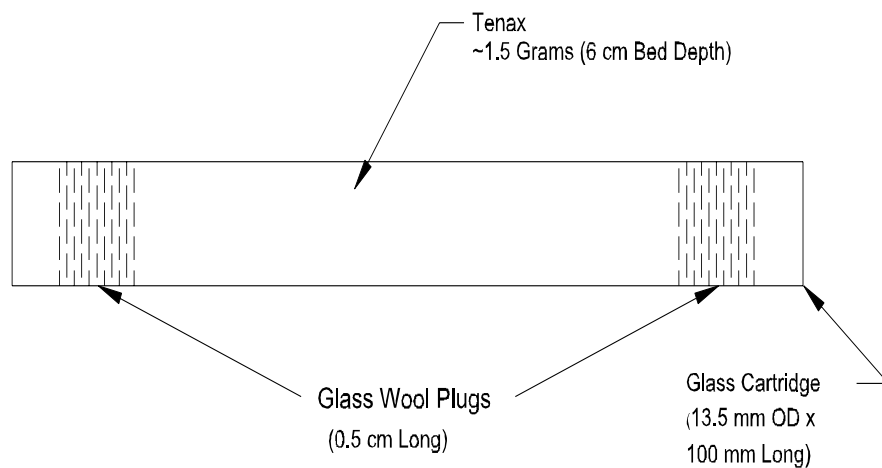
Figure 9-6 presents a diagram of a CMS trap construction and Figure 9-7 shows the GC/MS system used in analyzing the CMS cartridges.²⁸⁹ Air is drawn through a cartridge



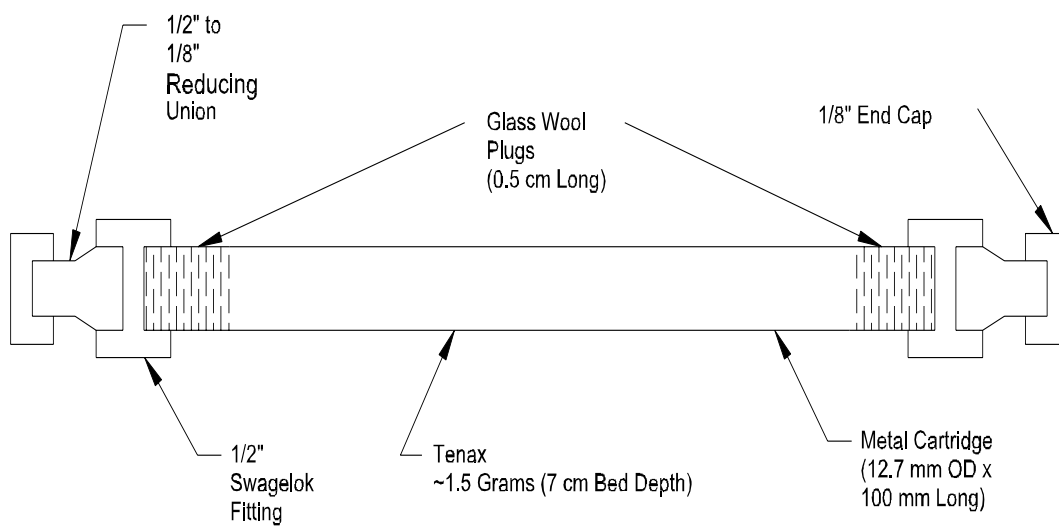
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Figure 9-4. Block Diagram of Analytical System for EPA Method TO-1

Source: Reference 289.



(a) Glass Cartridge



(b) Metal Cartridge

Figure 9-5. Typical Tenax® Cartridge

Source: Reference 289.

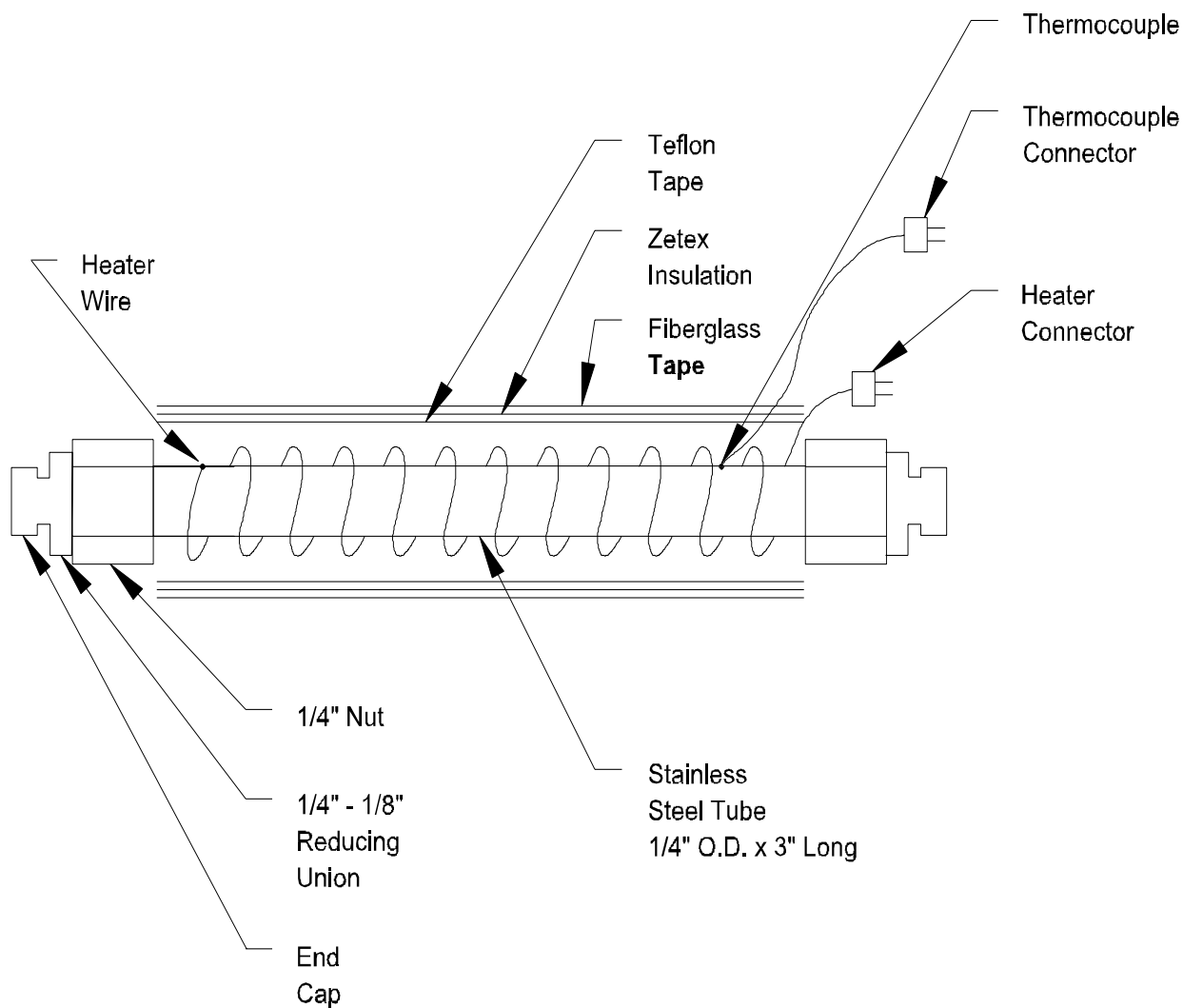


Figure 9-6. Carbon Molecular Sieve Trap (CMS) Construction

Source: Reference 289.

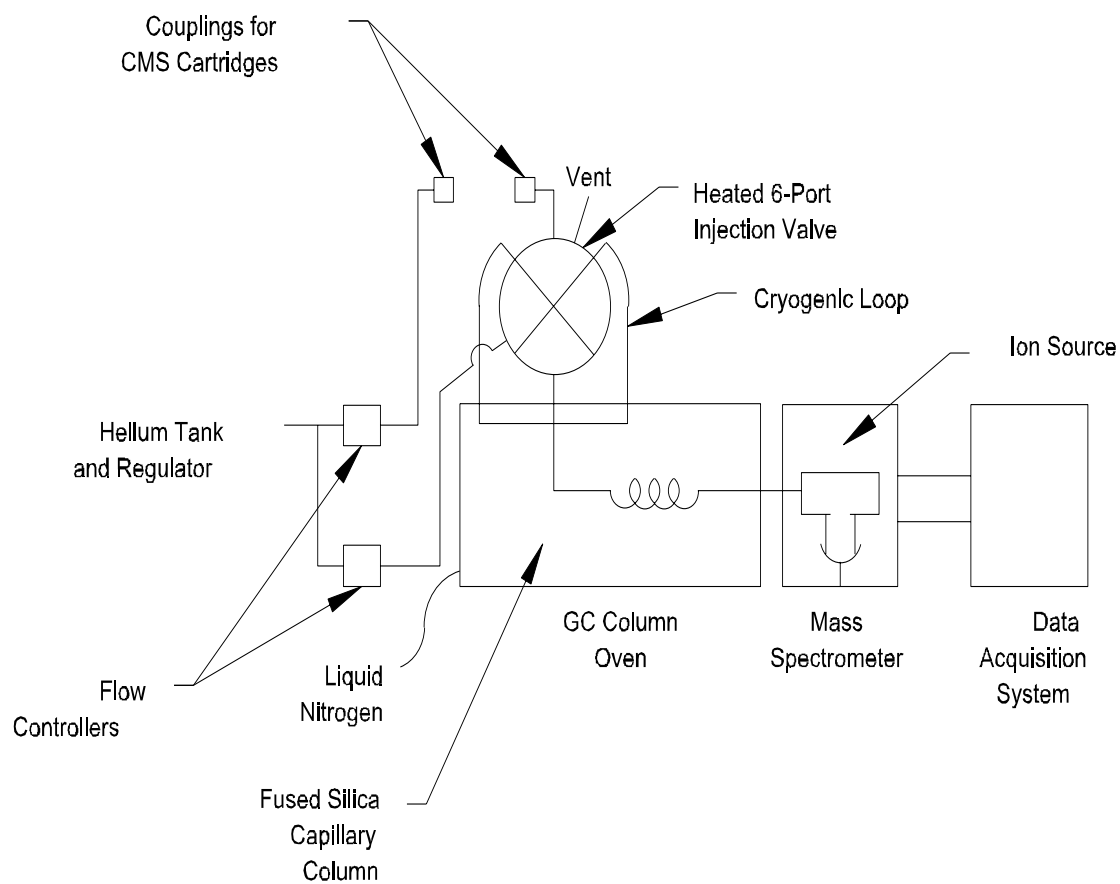


Figure 9-7. GC/MS Analysis System for CMS Cartridges

Source: Reference 289.

containing 0.4 g of a CMS adsorbent. The cartridge is analyzed in the laboratory by flushing with dry air to remove adsorbed moisture and purging the sample with helium while heating the cartridge to 350 to 400°C. The desorbed organics are collected in a cryogenic trap and flash-evaporated into a GC followed by an MS. Only capillary GC techniques should be used. The GC temperature is increased through a temperature program and the compounds are eluted from the column on the basis of boiling points. The MS identifies and quantifies the compounds by mass fragmentation patterns. Compound identification is normally accomplished using a library search routine on the basis of GC retention time and mass spectral characteristics. The most common interferences are structural isomers.

9.6 EPA METHOD TO-14^{283,289}

Ambient air concentrations of benzene can also be measured using EPA Method TO-14 from *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*.²⁸⁹ This method is based on collection of a whole-air sample in SUMMA® passivated stainless steel canisters and is used to determine semivolatile and volatile organic compounds.

This method is applicable to specific semivolatiles and VOCs that have been tested and determined to be stable when stored in pressurized and subatmospheric pressure canisters. Benzene has been successfully measured in the parts-per-billion- by-volume level using this method.

Figure 9-8 presents a diagram of the canister sampling system.²⁸⁹ Air is drawn through a sampling train into a pre-evacuated sample SUMMA® canister. The canister is attached to the analytical system. Water vapor is reduced in the gas stream by a Nafion dryer and VOCs are concentrated by collection into a cryogenically cooled trap. The cryogen is removed and the temperature of the sample raised to volatilize the sample into a high-resolution GC column. The GC temperature is increased through a temperature program and the compounds are eluted from the column on the basis of boiling points into a detector.

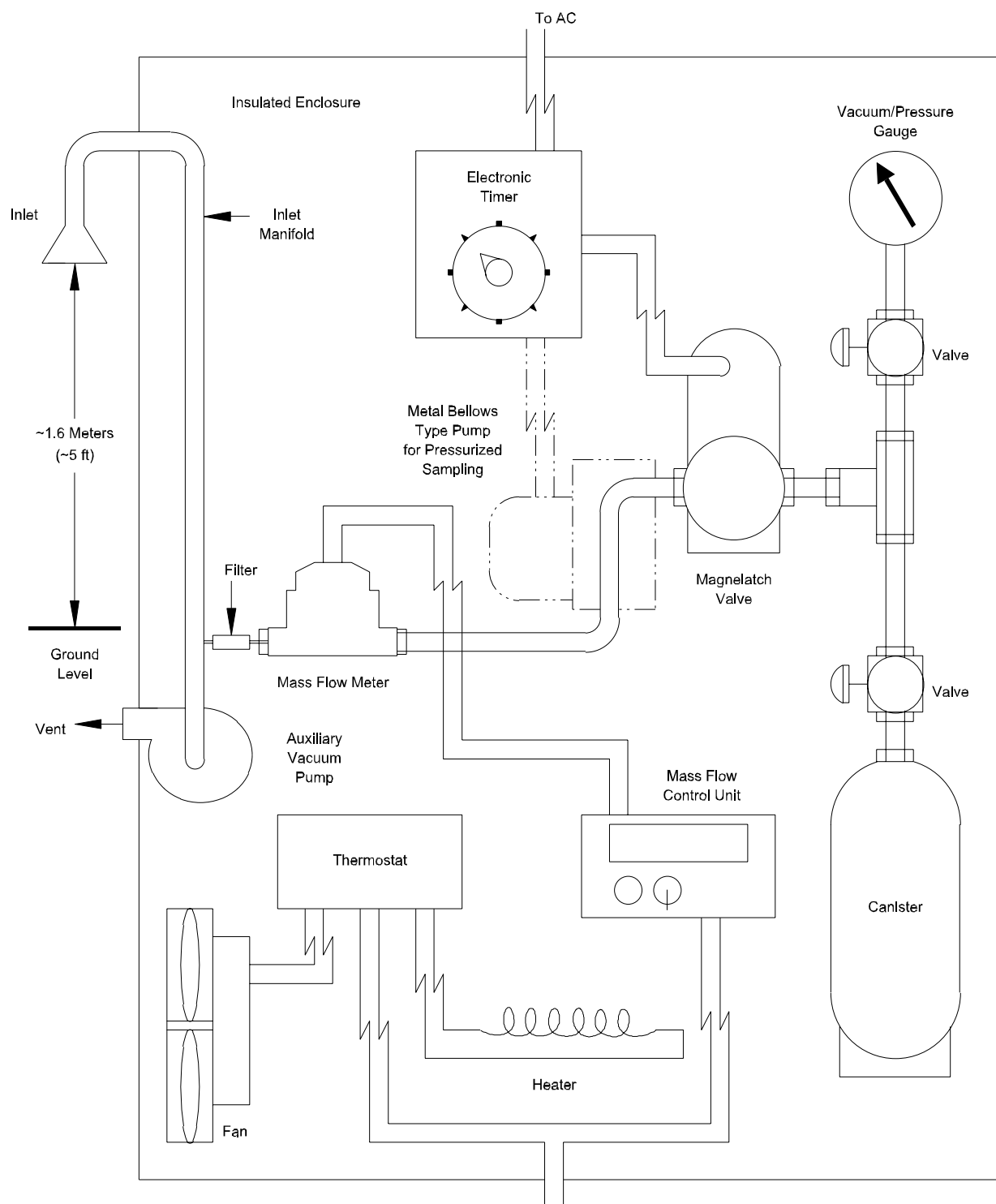


Figure 9-8. Sampler Configuration for EPA Method TO-14

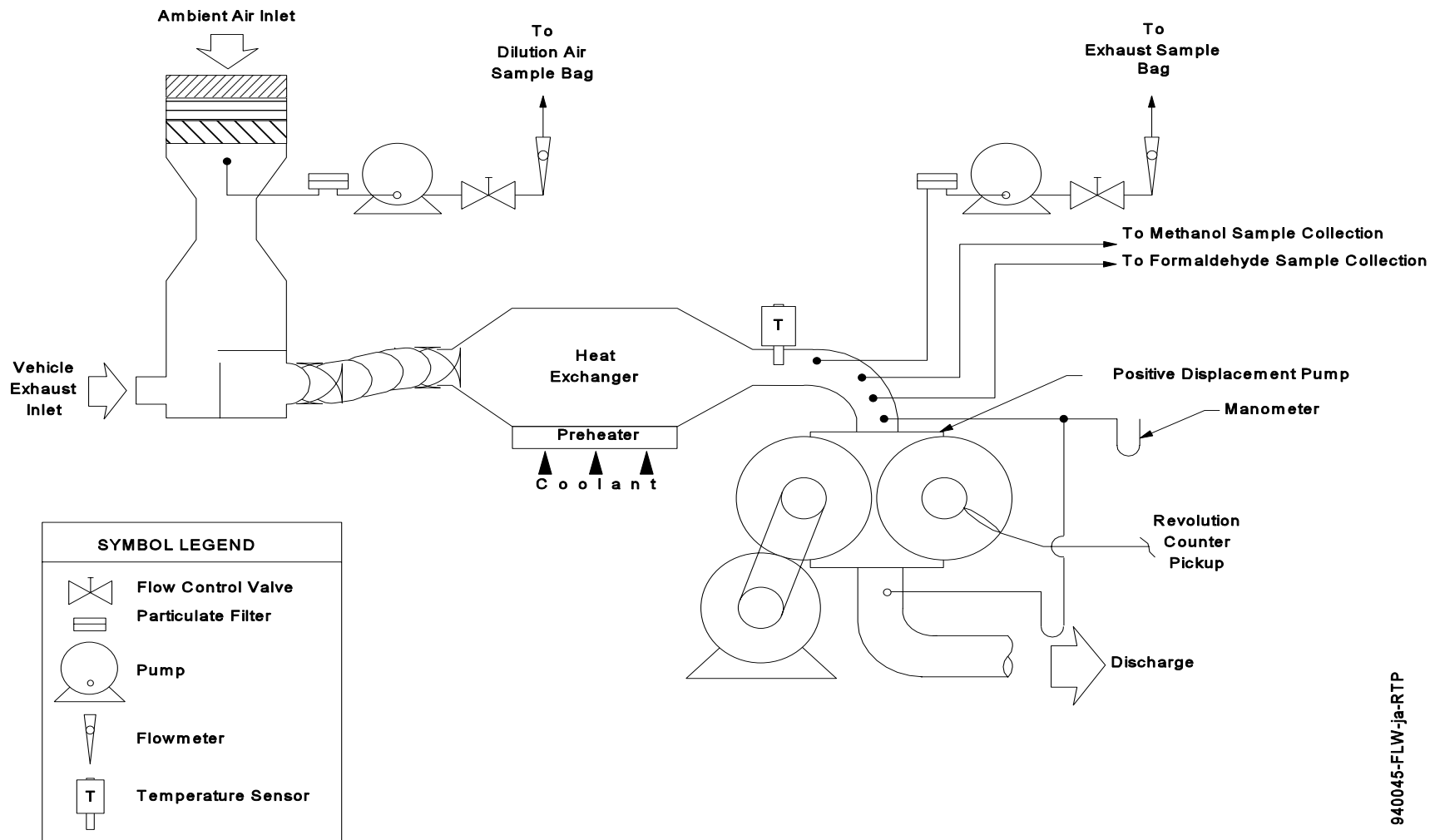
Source: Reference 289.

The choice of detector depends on the specificity and sensitivity required by the analysis. Non-specific detectors suggested for benzene analysis include flame ionization detectors (FID) with detection limits of about 4 ppbv and photoionization detectors (PID), which are about 25 times more sensitive than FID. Specific detectors include an MS operating in the selected ion mode or the SCAN mode, or an ion trap detector. Identification errors can be reduced by employing simultaneous detection by different detectors. The recommended column for Method TO-14 is an HP OV-1 capillary type with 0.32 mm I.D. and a 0.88 μ m cross-linked methyl silicone coating or equivalent. Samples should be analyzed within 14 days of collection. One of the advantages of Method TO-14 is that multiple analyses can be performed on one sample.

9.7 FEDERAL TEST PROCEDURE (FTP)

The most widely used test procedure for sampling emissions from vehicle exhaust is the FTP, which was developed in 1974.²⁹⁰⁻²⁹² The FTP uses the Urban Dynamometer Driving Schedule (UDDS), which is 1,372 seconds in duration. An automobile is placed on a chassis dynamometer, where it is run according to the following schedule: 505 seconds of a cold start; 867 seconds of hot transient; and 505 seconds of a hot start. (The definitions of the above terms can be found in the FTP description in the 40 CFR, Part 86).²⁹⁰ The vehicle exhaust is collected in Tedlar® bags during the three testing stages.

The most widely used method for transporting vehicle exhaust from the vehicle to the bags is a dilution tube sampling arrangement identical to the system used for measuring criteria pollutants from mobile sources.^{290,293} Dilution techniques are used for sampling auto exhaust because, in theory, dilution helps simulate the conditions under which exhaust gases condense and react in the atmosphere. Figure 9-9 shows a diagram of a vehicle exhaust sampling system.^{290,294} Vehicle exhausts are introduced at an orifice where the gases are collected and mixed with a supply of filtered dilution air. The diluted exhaust stream flows at a measured velocity through the dilution tube and is sampled isokinetically.



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Figure 9-9. Vehicle Exhaust Gas Sampling System

Source: Reference 290.

The major advantage to using a dilution tube approach is that exhaust gases are allowed to react and condense onto particle surfaces prior to sample collection, providing a truer composition of exhaust emissions as they occur in the atmosphere. Another advantage is that the dilution tube configuration allows simultaneous monitoring of hydrocarbons, CO, CO₂, and NO_x. Back-up sampling techniques, such as filtration/adsorption, are generally recommended for collection of both particulate- and gas-phase emissions.²⁹²

9.8 AUTO/OIL AIR QUALITY IMPROVEMENT RESEARCH PROGRAM SPECIATION METHOD

Although there is no EPA-recommended analytical method for measuring benzene from vehicle exhaust, the AQIRP method for the speciation of hydrocarbons and oxygenates is widely used.^{292,295} Initially, the AQIRP method included three separate analytical approaches for analyzing different hydrocarbons, but Method 3, the method designated for benzene, was dropped from use because of wandering retention times. Method 2 can be used to measure benzene from auto exhaust but some interferences, which will be discussed later, may occur.

This analytical method calls for analyzing the bag samples collected by the FTP method by injecting them into a dual-column GC with an FID. A recommended pre-column is a 2 m x 0.32 mm I.D. deactivated fused silica (J&W Scientific Co.) connected to an analytical column that is 60 m DB-1, 0.32 mm I.D., 1 µm film thickness.²⁹⁵ The detection limit for benzene with this method is 0.005 ppmC.

The peak areas corresponding to the retention times of benzene are measured and compared to peak areas for a set of standard gas mixtures to determine the benzene concentrations. However, there is a problem with benzene co-eluting with 1-methylcyclopentene. Therefore, the analyst should be aware of this potential interference.

The amount of benzene in a sample is obtained from the calibration curve in units of micrograms per sample. Collected samples are sufficiently stable to permit 6 days of ambient sample storage before analysis. If samples are refrigerated, they are stable for 18 days.